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Thermodynamics in Methanol Synthesis

Sometimes optimum temperature and pressure for a reaction at elevated temperature and pressure can be advantageously predicted thermodynamically. Such calculations yield not only valuable information on the optimum operational conditions but they may also indicate sensitivity of the process to changes in such conditions. An example is the synthesis of methanol from hydrogen and carbon monoxide.

Literature on Methanol Plants

Subject	Ref.
Temp. and press., 245–400° C. and 2200–1470 p.s.i. used	(1)
History of process, kinetics of reaction, and plant details; temp. and press., 300–375° C. and 270–350 atm.	(2)
300–400° C. as optimum temp.	(3)
Methanol plants in Germany	(5)

Little literature has appeared on optimum conditions for the methanol synthesis and the diversity of opinion is surprising when at least a dozen plants are operating in the United States.

The method described here for thermodynamically establishing optimum conditions for methanol synthesis is based on determination of pressure and temperature effects on heat of reaction and chemical equilibrium.

Temperature and Heat of Reaction

A general equation for chemical reaction is

$$aA + bB + = lL + mM + \quad (1)$$

Because heat capacity is an extensive property, its change in the system is

$$\Delta C_p = [l\,(C_p)_L + m(C_p)_M + \ldots.] - [a(C_p)_A + b(C_p)_B + \ldots.] \quad (2)$$

where C_p refers to molar heat capacities of the components. By considering the change in heat content of the system, the Kirchhoff equation (8) can be obtained, which on general integration gives

$$\Delta H_T = \Delta H_o + \int_{T_o}^{T} \Delta C_p\,.\,dT \quad (3)$$

where ΔH_o is the heat of reaction at T_o. Variation of heat capacity may be

$$C_p = \alpha + \beta T + \gamma T^2 + \delta T^3 + \quad (4)$$

where α, β, γ, and δ are empirical constants. C_p for the reaction may then be expressed as a function of temperature:

$$\Delta C_p = \Delta\alpha + \Delta\beta\,.\,T + \Delta\gamma\,.\,T^2 + \ldots. \quad (5)$$

where

$$\Delta\alpha = [l\,.\,\alpha_L + m\,.\,\alpha_M + \ldots.] - [a\,.\,\alpha_A + b\,.\,\alpha_B + \ldots.] \quad (6)$$

Similar equations can be obtained for the terms, α, β, γ, δ. When Equation 5 is substituted in Equation 3 and integrated,

$$\Delta H_T = \Delta H_o + [\Delta\alpha\,.\,T + {}^1/_2\,\Delta\beta\,.\,T^2 + {}^1/_3\,\Delta\gamma\,.\,T^3 + \ldots.]_{T_o}^{T}$$

or,

$$\Delta H_T = \Delta H_o + \Delta\alpha\,.\,T + {}^1/_2\Delta\beta\,.\,T^2 + {}^1/_3\Delta\gamma\,.\,T^3 - I_o \quad (7)$$

where I_o is the temperature integration constant. If ΔH is known at one temperature, the constant of integration can be combined with the constant value of ΔH_o to give a constant $(\Delta H_o - I_o)$, which can then be evaluated. In this way ΔH at any value of T may be obtained from Equation 7.

These derived equations can be applied to the methanol reaction,

$$CO_{(g)} + 2H_{2(g)} = CH_3OH_{(g)} \quad (8)$$

The heat of reaction at standard temperature and pressure is first calculated from published values (4) of heats of formation for the components:

$\Delta H_{25}°$ for $CH_3OH_{(g)}$ = −48100 cal.; for $CO_{(g)}$, −26400 cal.; and for $H_{2(g)}$, 0 (by convention).

Thus for the methanol reaction at 25° C. and 1 atm., $\Delta H_{25}°$ = −21700 cal. ΔC_p for the reaction is determined:

$$C_{p_{CH_3OH}} = 4.394 + 24.274 \times 10^{-3}T - 68.55 \times 10^{-7}T^2$$

$$C_{p_{H_2}} = 6.947 - 0.1995 \times 10^{-3}T + 4.81 \times 10^{-7}\,T_2$$

$$C_{p_{CO}} = 6.342 + 1.836 \times 10^{-3}T + 2.80 \times 10^{-7}T^2$$

These values were obtained from Dodge (2) and Ewell (3). Thus

$$\Delta C_p = C_{p_{CH_3OH}} - 2\,C_{p_{H_2}} - C_{p_{CO}} = -15.842 + 22.84 \times 10^{-3}\,T - 80.97 \times 10^{-7}T^2$$

and

$$\Delta\alpha = -15.842;\ \Delta\beta = 22.84 \times 10^{-3};\ \Delta\gamma = -80.97 \times 10^{-7}$$

Substituting these values in Equation 7,

$$\Delta H_T = (\Delta H_o - I_o) - 15.842\,T + 11.42 \times 10^{-3}\,T^2 - 26.99 \times 10^{-7}T^3$$

At 25° C. and 1 atm., ΔH_o = −21700 cal. This value can be substituted in the last equation to determine the constant $(\Delta H_o - I_o)$ as −17920. Thus,

$$\Delta H_T = -17920 - 15.84\,T + 11.42 \times 10^{-3}\,T^2 - 26.99 \times 10^{-7}\,T^3 \quad (9)$$

Heat of Reaction vs. Temperature

(Constant press., 1 atm.)

Temp., ° K.	ΔH_T, Cal./G.-Mole	Temp., ° C.	ΔH_T, Cal./G.-Mole
298.2	−21700	25	−21700
300	−21710	100	−22390
400	−22600	200	−23200
500	−23320	300	−23750
600	−23900	400	−24230
700	−24340	500	−24570
800	−24670	600	−24870
900	−24890	700	−25030
1000	−25040	800	−25100
1100	−25130	900	−25145
1200	−25150		

Derivation of Equation

A thermodynamic equation of state (7) expressed as

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \quad (10)$$

may be applied to each component in the methanol reaction, and an algebraic summation can be made, followed by integration. Thus,

$$\Delta H = \Delta H_o + \int_{P^0}^{P} \Delta V\,.\,dP - T\int_{P^0}^{P}\left(\frac{\partial(\Delta V)}{\partial T}\right)_P .\,dP \quad (11)$$

where

$$\Delta V = V_L + V_M - V_A - V_B \quad (12)$$

and where the standard state of each component is the pure substance at P^0.

Equation 10 indicates that if ideal conditions apply, then pressure will not affect heat of reaction because

$$PV = RT;\ \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P};\ V = RT/P$$

so that

$$\left(\frac{\partial H}{\partial P}\right)_T = 0$$

At elevated pressures, the conditions will not be ideal, and, therefore, pressure will affect heat of reaction. To determine this effect, an equation of state must be used in conjunction with Equation 11. For this study, the equation of Berthelot has been chosen. This equation explicit in P is

$$P.V = R.T\left[1 + \frac{9}{128}\frac{P.T_c}{P_c.T} \times \left(1 - 6\,\frac{T_c^2}{T^2}\right)\right] \ldots \quad (13)$$

where P_c, T_c, and V_c are the critical pressure, temperature, and molar volume, respectively.

Now $\Delta V = V_{CH_3OH} - V_{CO} - 2.V_{H_2}$ (14)

Combining Equations 13 and 14,

$$\Delta V = \frac{9}{128}R\left[\frac{T_{c_{CH_3OH}}}{P_{c_{CH_3OH}}}\left(1 - 6\frac{T_c^2{}_{CH_3OH}}{T^2}\right) - \frac{T_{c_{CO}}}{P_{c_{CO}}}\left(1 - 6\frac{T_c^2{}_{CO}}{T^2}\right) - 2\frac{T_{c_{H_2}}}{P_{c_{H_2}}}\times\left(1 - 6\frac{T_c^2{}_{H_2}}{T^2}\right)\right] - 2\frac{RT}{P} \quad (15)$$

Using Equation 15,

$$\int \Delta V.dP = \frac{9}{128}RP\left[\frac{T_{c_{CH_3OH}}}{P_{c_{CH_3OH}}}\left(1 - 6\frac{T_c^2{}_{CH_3OH}}{T^2}\right) - \frac{T_{c_{CO}}}{P_{c_{CO}}}\left(1 - 6\frac{T_c^2{}_{CO}}{T^2}\right) - 2\frac{T_{c_{H_2}}}{P_{c_{H_2}}}\times\left(1 - 6\frac{T_c^2{}_{H_2}}{T^2}\right)\right] - 2RT.\ln.P \quad (16)$$

and

$$\int\left(\frac{\partial(\Delta V)}{\partial T}\right)_P.dP = \frac{108}{128}\frac{RP}{T^3}\left[\frac{T_c^3{}_{CH_3OH}}{P_{c_{CH_3OH}}} - \frac{T_c^3{}_{CO}}{P_{c_{CO}}} - \frac{2T_c^3{}_{H_2}}{P_{c_{H_2}}}\right] - 2R.\ln.P \quad (17)$$

By combining Equations 11, 16, and 17,

$$\Delta H_{T.P} = \Delta H^\circ{}_{T.P^\circ} + \frac{9RP}{128}\left[\frac{T_{c_{CH_3OH}}}{P_{c_{CH_3OH}}} - \frac{T_{c_{CO}}}{P_{c_{CO}}} - \frac{2T_{c_{H_2}}}{P_{c_{H_2}}} + \frac{18}{T^2}\left(\frac{2T_c^3{}_{H_2}}{P_{c_{H_2}}} + \frac{T_c^3{}_{CO}}{P_{c_{CO}}} - \frac{T_c^3{}_{CH_3OH}}{P_{c_{CH_3OH}}}\right)\right]_{P^\circ}^{P} \quad (18)$$

The critical constants are given (*5*, *8*) and by substituting the values in Equation 18,

$$\Delta H_{T.P} = \Delta H_{T.P}{}^\circ - 0.5411\,P - \frac{3255000}{T^2}P \quad (19)$$

$\Delta H_{T.P}{}^\circ$ is a constant corresponding to 1 atm. of pressure, but having a different value at each temperature. This value is calculated at 1 atm. pressure by Equation 9. $\Delta H_{T.P}{}^\circ$'s are calculated at different temperatures in this way and when substituted in Equation 19, give a series of equations:

$$\Delta H_{TP} = \Delta H_{T.P}{}^\circ - mP \quad (20)$$

A general thermodynamic equation using van der Waal's equation has also been derived, and although it has not been used for methanol calculations, it should lead to the same result as the Berthelot equation (*11*).

Values of ΔH_{TP} are given in Figure 1 which shows clearly a range of stable optimum working conditions.

Equilibrium Constant

Equilibrium constant as a function of temperature can be calculated by

$$\Delta F^\circ = \Delta H^\circ - T.\Delta S^\circ \quad (21)$$

$$\Delta F^\circ = -RT.\ln.K_a \quad (22)$$

$$\frac{d\ln K_a}{dT} = \frac{\Delta H}{RT^2} \quad (23)$$

where ΔF° is free energy change of reaction; ΔS, entropy change of reaction; ΔH, heat capacity change in the reaction; T, absolute temperature; and K_a, equilibrium constant in terms of activities. Superscript zeros are change in free energy, heat content, and entropy when all reactants and products are in a standard state of unit activity.

Substituting Equation 7 in Equation 23.

$$\int d.\ln K_a = \int\left[\frac{\Delta H_o}{RT^2} + \frac{\Delta\alpha}{RT} + \frac{1}{2}\frac{\Delta\beta}{R} + \frac{1}{3}\frac{.\Delta\gamma.T}{R}\right]dT \quad (24)$$

Integrating Equation 24,

$$\ln.K_a = -\frac{\Delta H_o}{RT} + \frac{\Delta\alpha.\ln T}{R} + \frac{1}{2}\frac{\Delta\beta.T}{R} + \frac{1}{6}\frac{\Delta\gamma.T^2}{R} + C \quad (25)$$

Combining Equation 22 and 25,

$$\Delta F^\circ = \Delta H_o - \Delta\alpha.T\ln.T - \frac{1}{2}\Delta\beta.T^2 - \frac{1}{6}.\Delta\gamma.T^3 + I.T \quad (26)$$

where $I = -$R.C. Both I and C are integration constants and their values are determined from one known value of K_a or $F.^\circ$ If the specific heats of all the reacting substances are known accurately as a function of temperature, then one value of K_a will suffice to determine C and I. Thus, K_a can be expressed as a function of temperature.

For the methanol reaction, neglecting side reactions, K_a and T are related by

[Standard entropies in gram-cal./° K. (*5*, *6*, *9*, *10*)]

CH_3OH — 56.66 EU; CO — 47.32 EU; H_2 — 21.23 EU

Thus $\Delta S^\circ = -53.12$ EU

Using Equation 21 at 298.2 ° K.,

$$\Delta F^\circ = \Delta H^\circ - T.\Delta S^\circ = -21700 + (298.2 \times 53.12) = -5870$$

From the heat capacity equations and previously calculated ΔH at 25° C.,

$\Delta H_o = -17920$: $\Delta\alpha = -1584$: $\Delta\beta = 22.84 \times 10^{-3}$: $\Delta\gamma = -80.97 \times 10^{-7}$

Substituting these values, and the calculated value of ΔF in Equation 26, $I = -46.59$. The final equation for K_a as a function of temperature then is

$$\log_{10} K_a = \frac{3921}{T} - 7.971\log_{10} T + 0.002499\,T - 2.953 \times 10^{-7}\,T^2 + 10.20 \quad (27)$$

Substituting values for T in Equation 27, the results in Table I are obtained. Because the reaction is exothermic, the equilibrium becomes more unfavorable for methanol as the temperature increases. The considerations described apply to the reacting mixture at 1 atm. pressure. Although the equilibrium constant K_a is a function of temperature only, the equilibrium state of the system is strongly dependent on pressure.

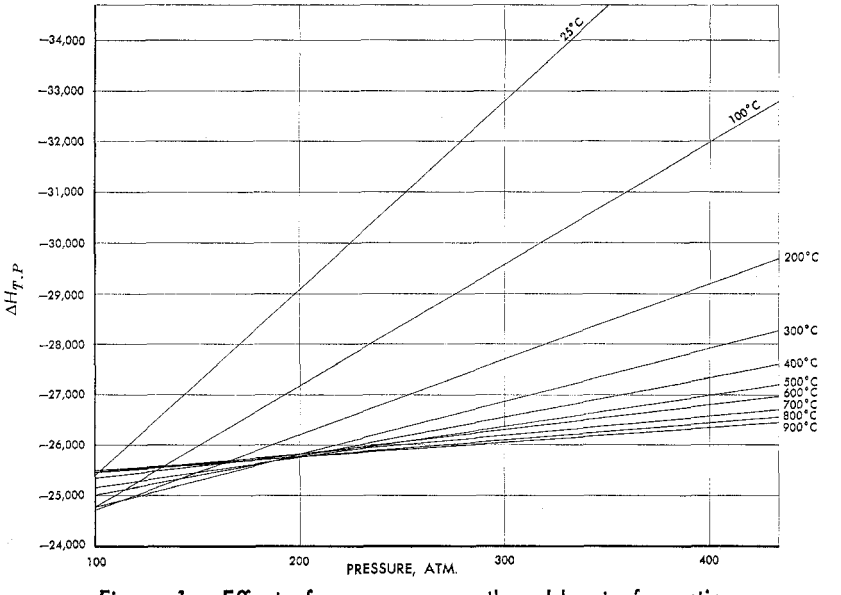

Figure 1. Effect of pressure on methanol heat of reaction

Pressure Equilibrium Constants

Considering Equation 1, the equilibrium constant in terms of activities is

$$K_a = \frac{a_L{}^l \times a_M{}^m \times \cdots}{a_A{}^a \times a_B{}^b \times \cdots} \quad (28)$$

If the standard state of unit activity is the state of unit fugacity, then activity of each reacting component can be replaced by its fugacity, so that the equation of the equilibrium constant becomes

$$K_f = \frac{f_L{}^l \times f_M{}^m \times \cdots}{f_A{}^a \times f_B{}^b \times \cdots} \quad (29)$$

where f is fugacity. Now $f/p = \gamma$ where γ is fugacity coefficient, and p is partial

pressure. Thus substituting for the fugacities in Equation 29:

$$K_f = \frac{p_L{}^l \times p_M{}^m \times \ldots \gamma_L{}^l \times \gamma_M{}^m \times \ldots}{p_A{}^a \times p_B{}^b \times \ldots \gamma_A{}^a \times \gamma_B{}^b \times \ldots} \quad (30)$$

Data for determining fugacities of individual gases in mixtures are generally not available; an approximation is: $f \cong nf'$, where f is fugacity of the component in the gaseous mixture; f', fugacity of the pure component at the total pressure; and n, mole fraction of the component in the mixture. If $\gamma' = f'/P$, then the expression for the equilibrium constant becomes

$$K_{f'} = \frac{n_L^l \times n_M^m}{n_A^a \times n_B^b} \cdot \frac{\gamma''_L \times \gamma'^m_M}{\gamma'^a_A \times \gamma'^b_B} \cdot P^{\Delta N} \quad (31)$$

where ΔN is the change in the number of moles in the reaction.

$$\Delta N = (l + m + \ldots) - (a + b + \ldots) \quad (32)$$

and $K_{f'}$ shows that Equation 31 is based on an approximation. And hence $K_{f'}$ cannot be exactly constant combining the first and third factors of Equation 31, $K_{p'} = K_n \times P^{\Delta N}$. Thus

$$K_{f'} = K_{p'} \times K_{\gamma'} \quad (33)$$

At low pressures where the gases may be assumed as ideal, then $K_{\gamma'} = 1$, and $K_{p'} = K_{f'}$. At higher pressures, however, $K_{p'}$ is not constant, and to calculate it, both $K_{f'}$ and $K_{\gamma'}$ must be known. Newton (*8*) evaluated γ' for a number of gases from experimental PVT data, and published a set of curves of universal activity coefficients. As these curves were based on experimental data, they provide a convenient and accurate source of fugacities and activity coefficients for gases. To calculate the effect of pressure at any temperature on the methanol reaction, it is necessary to evaluate the reduced temperatures and pressures. The critical values are given (*4*) for methanol, hydrogen, and carbon monoxide. From these values the reduced temperatures and pressures were calculated in each case for each component. Newton (*8*) suggested that for some gases, such as hydrogen, better universal reduced curves could be obtained if the reduced values were calculated:

$$T_r = \frac{T}{T_c + 8} \qquad P_r = \frac{P}{P_c + 8}$$

These values were used for hydrogen. Knowing T and P in each case, the values of γ' were found from Newton's universal graphs. In this way, the effect of pressure on $K_{\gamma'}$ at any temperature can be determined.

$K_{f'}$ is a function of temperature only, and independent of pressure. However, the equilibrium state of a system is strongly dependent on pressure as is reflected in the values of $K_{p'}$. As $K_{f'}/K_{\gamma'}$

Table I. K_a as a Function of Temperature

T° C.	0	100	200	300	400	500
K_a	677300	12.92	1.909×10^{-2}	2.42×10^{-4}	1.079×10^{-6}	1.015×10^{-6}
T° C.	600		700	800	900	
K_a	1.610×10^{-7}		3.642×10^{-8}	1.112×10^{-8}	4.052×10^{-9}	

Table II. $K_{p'}$ as a Function of Pressure and Temperature

		CH_3OH		H_2		CO			
		T_r							
T,° C.	P,	0.73		9.05		2.78			
100	Atmos.	P_r	γ	P_r	γ	P_r	γ	K_γ	$K_{p'}$
	100	1.01	..	4.81	1.06	2.89	1.02		
	200	2.02	..	9.62	1.11	5.78	1.05		
	300	3.03	..	14.43	1.17	8.67	1.10		
	400	4.04	..	19.24	1.24	11.56	1.17		
	500	5.05	..	24.05	1.32	14.45	1.24		
	600	6.06	..	28.86	1.36	17.34	1.33		
	700	7.07	..	33.67	1.44	20.23	1.42		
	800	8.08	..	38.84	1.53	23.12	1.56		
	900	9.09	..	43.29	1.60	26.01	..		
	1000	10.10	..	48.10	1.70	28.90	..		
		T_r						K_γ	K_p
200		0.92		11.49		3.52		($\times 10^{-2}$)	($\times 10^{-2}$)
	100	1.01	0.52	4.81	1.05	2.89	1.04	45.3	4.21
	200	2.02	0.34	9.62	1.08	5.78	1.09	29.2	6.53
	300	3.03	0.26	14.43	1.13	8.67	1.15	17.7	10.80
	400	4.04	0.22	19.24	1.18	11.56	1.29	13.0	14.67
	500	5.05	0.19	24.05	1.23	14.45	1.38	9.75	19.60
	600	6.06	0.18	28.86	1.29	17.34	1.46	7.83	24.35
	700	7.07	0.17	33.67	1.35	20.23	1.58	6.40	29.80
	800	8.08	0.16	38.48	1.40	23.12	..	5.17	36.85
	900	9.09	0.16	43.29	1.46	26.01	..	...	...
	1000	10.10	0.17	48.10	1.54	28.90	..	...	...
		T_r						K_γ	K_p
300		1.12		13.92		4.26		($\times 10^{-2}$)	($\times 10^{-4}$)
	100	1.01	0.76	4.81	1.04	2.89	1.04	67.6	3.58
	200	2.02	0.60	9.62	1.07	5.78	1.08	48.6	4.97
	300	3.03	0.47	14.43	1.11	8.67	1.13	33.8	7.15
	400	4.04	0.40	19.24	1.15	11.56	1.20	25.2	9.60
	500	5.05	0.37	24.05	1.20	14.45	1.27	20.2	11.98
	600	6.06	0.34	28.86	1.24	17.34	1.34	16.5	14.65
	700	7.07	0.33	33.67	1.29	20.23	1.44	13.8	17.54
	800	8.08	0.34	38.48	1.34	23.12	1.52	12.5	19.35
	900	9.09	0.34	43.29	1.38	26.01	1.62	11.0	22.00
	1000	10.10	0.35	48.10	1.44	28.90	1.72	9.84	24.60
		T_r						K_γ	K_p
400		1.31		16.35		5.01		($\times 10^{-2}$)	($\times 10^{-5}$)
	100	1.01	0.88	4.81	1.04	2.89	1.04	78.2	1.378
	200	2.02	0.77	9.62	1.07	5.78	1.08	62.5	1.726
	300	3.03	0.68	14.43	1.10	8.67	1.12	50.2	2.075
	400	4.04	0.62	19.24	1.14	11.56	1.19	40.0	2.695
	500	5.05	0.58	24.05	1.17	14.45	1.26	33.6	3.210
	600	6.06	0.56	28.86	1.22	17.34	1.34	28.5	5.780
	700	7.07	0.55	33.67	1.25	20.23	1.40	25.1	4.295
	800	8.08	0.55	38.48	1.29	23.12	1.48	22.3	4.830
	900	9.09	0.55	43.29	1.33	26.01	1.57	19.8	5.450
	1000	10.10	0.56	48.10	1.38	28.90	1.65	17.8	6.050
		T_r						K_γ	K_p
500		1.50		18.80		5.75		($\times 10^{-2}$)	($\times 10^{-6}$)
	100	1.01	0.92	4.81	1.03	5.75	1.04	83.5	1.215
	200	2.02	0.86	9.62	1.06	5.78	1.07	71.5	1.420
	300	3.03	0.80	14.43	1.09	8.67	1.14	59.0	1.720
	400	4.04	0.76	19.24	1.11	11.56	1.19	51.9	1.960
	500	5.05	0.74	24.05	1.14	14.45	1.25	45.5	2.230
	600	6.06	0.72	28.86	1.18	17.34	1.30	39.8	2.550
	700	7.07	0.71	33.67	1.21	20.23	1.36	35.7	2.842
	800	8.08	0.71	38.48	1.24	23.12	1.42	32.5	3.120
	900	9.09	0.72	43.29	1.27	26.01	1.50	29.8	3.400
	1000	10.10	0.73	48.10	1.34	28.90	1.56	26.1	3.890

Table II. $K_{p'}$ as a Function of Pressure and Temperature (*Continued*)

T, °C.	P,	CH_3OH T_r = 1.70		H_2 T_r = 21.20		CO T_r = 6.49		K_γ ($\times 10^{-2}$)	K_p ($\times 10^{-7}$)
600	Atmos.	P_r	γ	P_r	γ	P_r	γ		
	100	1.01	0.96	4.81	1.02	2.89	1.01	88.8	1.81
	200	2.02	0.92	9.62	1.05	5.78	1.07	78.0	2.065
	300	3.03	0.88	14.43	1.08	8.67	1.11	68.0	2.365
	400	4.04	0.86	19.24	1.11	11.56	1.16	60.1	2.675
	500	5.05	0.84	24.05	1.14	14.45	1.21	53.6	3.000
	600	6.06	0.83	28.86	1.17	17.34	1.26	48.1	3.345
	700	7.07	0.83	33.67	1.20	20.23	1.32	43.7	3.680
	800	8.08	0.83	38.48	1.24	23.12	1.37	39.4	4.080
	900	9.09	0.84	43.29	1.28	26.01	1.45	35.3	4.550
	1000	10.10	0.85	48.10	1.32	28.90	1.54	31.7	5.070
		T_r						K_γ	K_p
700		1.90		23.65		7.24		($\times 10^{-2}$)	($\times 10^{-8}$)
	100	1.01	0.97	4.81	1.02	2.89	1.04	89.7	4.06
	200	2.02	0.94	9.62	1.04	5.78	1.07	81.2	4.48
	300	3.03	0.92	14.43	1.06	8.67	1.11	73.7	4.94
	400	4.04	0.90	19.24	1.08	11.56	1.15	67.1	5.43
	500	5.05	0.89	24.05	1.11	14.45	1.19	60.7	6.00
	600	6.06	0.89	28.86	1.13	17.34	1.24	56.1	6.49
	700	7.07	0.96	33.67	1.14	20.23	1.28	51.5	7.07
	800	8.08	0.97	38.48	1.16	23.12	1.32	48.3	7.53
	900	9.09	0.91	43.29	1.22	26.01	1.40	43.7	8.34
	1000	10.10	0.93	48.1	1.24	28.90	1.44	42.0	8.67
		T_r						K_γ	K_p
800		2.10		26.10		7.97		($\times 10^{-2}$)	($\times 10^{-8}$)
	100	1.01	0.98	4.81	1.02	2.89	1.03	91.5	1.215
	200	2.02	0.97	9.62	1.03	5.78	1.06	85.8	1.295
	300	3.03	0.96	14.43	1.05	8.67	1.10	78.7	1.412
	400	4.04	0.95	19.24	1.07	11.56	1.14	72.7	1.530
	500	5.05	0.95	24.05	1.09	14.45	1.18	67.8	1.640
	600	6.06	0.96	28.86	1.12	17.34	1.23	61.8	1.800
	700	7.07	0.96	33.67	1.14	20.23	1.28	57.7	1.928
	800	8.08	0.97	38.48	1.16	23.12	1.32	54.7	2.035
	900	9.09	0.98	43.29	1.18	26.01	1.37	51.4	2.325
	1000	10.10	1.00	48.10	1.21	28.90	1.43	47.8	2.325
		T_r						$K\gamma$	K_p
900		2.29		28.50		8.72		($\times 10^{-2}$)	($\times 10^{-9}$)
	100	1.01	0.99	4.81	1.02	2.89	1.03	92.4	4.39
	200	2.02	0.99	9.62	1.03	5.78	1.06	88.0	4.61
	300	3.03	0.99	14.43	1.05	8.67	1.10	81.6	4.97
	400	4.04	0.99	19.24	1.07	11.56	1.13	76.6	5.29
	500	5.05	0.99	24.05	1.08	14.45	1.17	72.5	5.59
	600	6.06	0.99	28.86	1.10	17.34	1.21	67.6	6.00
	700	7.07	1.00	33.67	1.12	20.23	1.25	63.8	6.35
	800	8.08	1.02	38.48	1.15	23.12	1.29	59.8	6.77
	900	9.09	1.04	43.29	1.17	26.01	1.33	57.2	7.08
	1000	10.10	1.06	48.10	1.19	28.90	1.36	55.0	7.36

$= K_{p'}$, and if $K_{f'}$, which is a constant is determined for one case, then once the values of $K_{\gamma'}$ are determined by means of Newtons universal graphs, it will be possible to calculate $K_{p'}$ as a function of pressure at any temperature (Table II).

In some cases, the value of γ' could not be obtained without introducing uncertainty, and blank spaces have been left in the table when such situations arise.

Conclusions

Heat of the methanol reaction increases with pressure, and because the reaction is exothermic, then by the LeChatelier-Braun effect, temperature should be kept as low as is practical for a maximum yield of methanol. For large converters with integral heat exchange systems, hot spots may develop in the catalyst mass, and become hot enough (about 400° C.) to produce methanization, which may cause both product losses and enforce shutdown by converter runaway. Conversion increases rapidly with pressure. K_n increases rapidly with pressure, but the effect is enhanced by the fact that $K_{\gamma'}$ becomes smaller with increasing pressure.

At about 250 atm. of pressure, heat of reaction is virtually independent of temperature. Fluctuations around a working temperature of 300° C. would produce little effect on heat of reaction. This is significant because a process operated in this region may be more easily controlled. These calculated values agree with values quoted (*2*) under practical conditions.

This thermodynamic study for methanol synthesis should be useful for predicting optimum values of temperature and pressure for new processes. It can be useful also for checking operating conditions of existing processes.

Nomenclature

a = moles of component A
b = moles of component B
C = integration constant
C_p = heat capacity, cal./gram-mole/° K.
F = free energy, cal./gram-mole
ΔH = heat of reaction, cal./gram-mole
$\Delta H_o, \Delta H_T$ = heat of reaction at T_o° K. and T° K., respectively, cal./gram-mole
ΔH_T° = heat of formation at T° K.
I_o = temperature integration constant
I = integration constant
$K_a, K_f, K_n, K_p, K_\gamma$ = equilibrium constant, in terms of activities, fugacities, moles, partial pressures, and fugacity coefficients, respectively
l, m = moles of component L, and M, respectively
n = mole fraction of any component in a mixture
p = partial pressure, atm.
P = pressure, atm.
P_c = critical pressure, atm.
P_r = reduced pressure, atm.
R = gas constant, cal./° K./mole
S = entropy, cal./° K.
T = absolute temperature, ° K.
T_c = critical temperature, ° K.
T_r = reduced temperature, ° K.
V = molal vol., cc./gram-mole
$\alpha, \beta, \gamma, \delta$ = empirical constants
γ = fugacity coefficient

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